Theor Chem Acc (2002) 108:21–26
DOI 10.1007/s00214-002-0341-2

Theoretical
Chemistry Accounts

Regular article

Use of addition theorems in evaluation of multicenter nuclear-attraction and electron-repulsion integrals with integer and noninteger *n* Slater-type orbitals

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Received: 13 February 2002 / Accepted: 11 March 2002 / Published online: 4 July 2002

Abstract. Multicenter integrals appearing in the Hartree–Fock–Roothaan equations for molecules are calculated using different kinds of series expansion formulas obtained from the expansions of integer and noninteger *n* Slater-type orbitals, in terms of Ψ^{α}-exponential-type orbitals (where $\alpha = 1, 0, -1, -2, \ldots$) at a displaced center, that form complete orthonormal sets and are represented by linear combinations of integer *n* Slater-type orbitals. The convergence of these series is tested by calculating concrete cases. The accuracy of the results is quite high for quantum numbers, screening constants, and location of orbitals.

Key words: Slater-type orbitals – Addition theorems – Nuclear-attraction integrals – Electron-repulsion integrals – Noninteger principal quantum numbers

1 Introduction

In the treatment of multicenter integrals it is often necessary to transform operators and Slater-type orbitals (STOs), which depend upon the coordinates of two particles, in such a way that the coordinates of the pertaining particles appear in a computationally more convenient form. In most cases this requires a separation of variables which can be accomplished with the help of so-called addition theorems. Probably the best-known example of addition theorems for operators is the Laplace expansion of the Coulomb potential,

$$\frac{1}{r_{21}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} S_{lm}^*(\theta_2, \varphi_2) S_{lm}(\theta_1, \varphi_1) \ , \tag{1}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. Here the spherical harmonics $S_{\rm lm}$ are determined by the relation

$$S_{lm}(\theta, \phi) = P_{l|m|}(\cos\theta)\Phi_m(\phi) \ , \tag{2}$$

where $P_{\rm l|m|}$ are normalized associated Legendre functions. For complex spherical harmonics $S_{\rm lm}(\theta,\varphi) \equiv Y_{\rm lm}(\theta,\varphi)$,

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \tag{3}$$

and for real spherical harmonics

$$\Phi_m(\phi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} \begin{cases} \cos|m|\phi & for\ m \geq 0 \\ \sin|m|\phi & for\ m < 0 \end{cases} \ . \tag{4}$$

It should be noted that our definition of phases for complex spherical harmonics $Y^*_{lm} = Y_{\rm l-m}$ differs from the Condon–Shortley phases [1] by the sign factor.

The earliest approaches for the evaluation of multicenter integrals consisted of using the relatively complicated addition theorems of STOs to separate the integration variables from those related to the geometry of the molecule [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18]. The great progress made in both applied mathematics and computer science has led a number of researchers to focus their efforts on the elaboration of new approaches directed to computing multicenter integrals over STOs. Unfortunately, they also were not entirely successful. To our knowledge, many authors; (see Refs. [19, 20, 21, 22, 23] and references therein) have addressed this problem and although many improvements have been made in the past few years by the use of computers, an efficient general program for the calculation of multicenter integrals over STOs is not yet available. We have had considerable success in using the addition theorems in the evaluation of multicenter molecular integrals. In previous work [24], by the use of complete orthonormal sets of Ψ^{α}-exponential-type orbitals (ETOs), where $\alpha = 1, 0, -1, -2, \ldots$, all the multicenter multielectron integrals with integer and noninteger *n* STOs (ISTOs and NISTOs) were expressed in terms of overlap integrals between the basis functions and the ISTOs being translated. For the calculation of overlap integrals of ISTOs and NISTOs efficient computer programs are available in our group [25, 26, 27, 28].

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Therefore, by using the computer programs for the overlap integrals one can calculate the arbitrary multicenter integrals with ISTOs and NISTOs appearing in the determination of various properties for molecules when the Hartree–Fock–Roothaan approximation is employed.

For obtaining the expansion of STOs about a new center one of us in Ref. [24] introduced the new complete orthonormal sets of Ψ^{α}-ETOs defined by

$$\Psi^{\alpha}_{nlm}(\zeta,\vec{r}) = (-1)^{\alpha}\left(\frac{(2\zeta)^{3}(n-l-1)!}{(2n)^{\alpha}[(n+l+1-\alpha)!]^{3}}\right)^{1/2} (2\zeta r)^{l}\mathrm{e}^{-\zeta r}L^{2l+2-\alpha}_{n+l+1-\alpha}(2\zeta r)S_{lm}(\theta,\varphi) \ , \tag{5}$$

where $\alpha = 1,\ 0,\ -1,\ -2,\ -3\ldots$. Here $L^{p}_{q}(x)$ are the generalized Laguerre polynomials. We notice that the arbitrary multicenter multielectron molecular integrals can be calculated using different kinds of translation formulas for the STOs obtained in Ref. [24] from the expansion of STOs, in terms of Ψ^{α}-ETOs at a displaced center, that form complete orthonormal sets and are represented by linear combinations of STOs.

In the Hartree–Fock–Roothaan equations for molecules, the matrix elements of nuclear-attraction and electron-repulsion operators between the determinantal wave functions of molecules are expressed through the multicenter integrals with the same operators. The multicenter nuclear-attraction and electron-repulsion integrals over STOs examined in this work have the following form:

$$I_{p_1^{*}p_1^{\prime *}}(\zeta_1,\zeta_1';\vec{R}_{ca},\vec{R}_{ab}) = \int \chi^{*}_{p_1^{*}}(\zeta_1,\vec{r}_{a1})\chi_{p_1^{\prime *}}(\zeta_1',\vec{r}_{c1})\frac{1}{r_{b1}}\mathrm{d}V_1 \ , \tag{6}$$

$$\begin{aligned} I_{p_1^{*}p_1^{\prime *};p_2^{*}p_2^{\prime *}}&(\zeta_1,\zeta_1',\zeta_2,\zeta_2';\vec{R}_{ca},\vec{R}_{ba},\vec{R}_{da}) \\ &= \int \chi^{*}_{p_1^{*}}(\zeta_1,\vec{r}_{a1})\chi_{p_1^{\prime *}}(\zeta_1',\vec{r}_{c1}) \\ &\qquad \times \frac{1}{r_{21}}\chi_{p_2^{*}}(\zeta_2,\vec{r}_{b2})\chi^{*}_{p_2^{\prime *}}(\zeta_2',\vec{r}_{d2})\mathrm{d}V_1\mathrm{d}V_2 \ , \end{aligned} \tag{7}$$

where $p_i^{*} \equiv n_i^{*}l_im_i, p_i^{\prime *} \equiv n_i^{\prime *}l_i'm_i', \vec{R}_{gh} = \vec{R}_h - \vec{R}_g, \vec{r}_{gi} = \vec{r}_i - \vec{R}_g$ $(i = 1,2\ \text{and}\ g = a,b,c,d)$ $\vec{r}_i$ and $\vec{R}_g$ are the radius vectors of the electron and the nucleus relative to the molecule-fixed axes centered at a reference origin O, and $\chi_{p_i^{*}}(\zeta_i,\vec{r}_{gi})$ and $\chi_{p_i^{\prime *}}(\zeta_i',\vec{r}_{hi})$ are the normalized complex or real NISTOs centered on the nuclei *g and h*, respectively:

$$\chi_{n^{*}lm}(\zeta,\vec{r}) = (2\zeta)^{n^{*}+\frac{1}{2}}[\Gamma(2n^{*}+1)]^{-\frac{1}{2}}r^{n^{*}-1}\mathrm{e}^{-\zeta r}S_{lm}(\theta,\varphi) \ . \tag{8}$$

Here $\Gamma(x)$ denotes the gamma function [29]. The normalized ISTOs can be obtained from Eq. (7) for $n^{*} = n$, where n is an integer:

$$\chi_{nlm}(\zeta,\vec{r}) = (2\zeta)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{n-1}\mathrm{e}^{-\zeta r}S_{lm}(\theta,\varphi) \ . \tag{9}$$

The aim of this report is, by the use of addition theorems for $\frac{1}{r_{21}}$ and ISTOs, to obtain the series expansion formulas for the multicenter nuclear-attraction and electron-repulsion integrals through the overlap integrals with the arbitrary integer and noninteger values of principal quantum numbers of STOs. We notice that the method used in this work is an extension of the results of Refs. [30, 31] to the case of NISTOs in which the formulas for the multicenter integrals over ISTOs have been established.

2 Use of addition theorem for STOs

In order to evaluate multicenter nuclear-attraction and electron-repulsion integrals, we use in Eqs. (6) and (7) the series expansion formulas for NISTOs, obtained using Ψ^{α}-ETOs, where $\alpha = 1,\ 0,\ -1,\ -2,\ldots$, in terms of ISTOs at a displaced center [24]:

$$\chi_{n^{*}lm}(\zeta,\vec{r}_a) = \lim_{N\to\infty}\sum_{\mu=1}^{N}\sum_{\nu=0}^{\mu-1}\sum_{\sigma=-\nu}^{\nu} V^{\alpha N*}_{n^{*}lm,\mu\nu\sigma}(\zeta,\zeta;\vec{R})\chi_{\mu\nu\sigma}(\zeta,\vec{r}_b) \ , \tag{10}$$

where $\vec{R} \equiv \vec{R}_{ab}$ and the expansion coefficients $V^{\alpha N}$ are determined as follows:

$$V^{\alpha N}_{n^{*}lm,\mu\nu\sigma}(\zeta,\zeta;\vec{R}) = \sum_{\mu'=\nu+1}^{N}\Omega^{\alpha\nu}_{\mu\mu'}(N)S_{n^{*}lm,\mu'-\alpha\nu\sigma}(\zeta,\zeta;\vec{R}) \ , \tag{11}$$

$$\Omega^{\alpha\nu}_{\mu\kappa}(N) = \left(\frac{[2(k-\alpha)]!}{(2\kappa)!}\right)^{\frac{1}{2}}\sum_{\mu'=\max(\mu,\kappa)}^{N}(2\mu')^{\alpha}\omega^{\alpha\nu}_{\mu\mu'}\omega^{\alpha\nu}_{\mu'\kappa} \ , \tag{12}$$

$$\begin{aligned} \omega^{\alpha\nu}_{\mu\mu'} = (-1)^{\mu'-\nu-1}\Bigg(&\frac{(\mu'+\nu+1)!}{(2\mu)^{\alpha}(\mu'+\nu+1-\alpha)!} \\ &\times F_{\mu'+\nu+1-\alpha}(\mu+\nu+1-\alpha)F_{\mu'-\nu-1}(\mu-\nu-1) \\ &\times F_{\mu'-\nu-1}(2\mu')\Bigg)^{1/2} \ . \end{aligned} \tag{13}$$

Here $F_{\mu}(k) = k!/[\mu!(k-\mu)!]$ and the quantities $S_{n^{*}lm,\mu\nu\sigma}$ are the overlap integrals between the normalized NISTOs and ISTOs:

$$S_{n^{*}lm,\mu\nu\sigma}(\zeta,\zeta;\vec{R}) = \int \chi^{*}_{n^{*}lm}(\zeta,\vec{r}_a)\chi_{\mu\nu\sigma}(\zeta,\vec{r}_b)\mathrm{d}V \ . \tag{14}$$

We notice that for $\vec{R}_{ab} = 0$ the expansion coefficients $V^{\alpha N}$ are reduced to the Konecker symbol, i.e.,

$$V^{\alpha N}_{n^{*}lm,\mu\nu\sigma}(\zeta,\zeta;0) = \delta_{N\mu}\delta_{\mu n^{*}}\delta_{\nu l}\delta_{\sigma m} \ . \tag{15}$$

Taking into account the addition theorem (Eq. 10) in Eqs. (6) and (7) we obtain the following series expansion formulas in terms of two-center nuclear-attraction and one-center electron-repulsion integrals:

$$\begin{aligned} I_{p_1^{*}p_1^{\prime *}}(\zeta_1,\zeta_1';\vec{R}_{ca},\vec{R}_{ab}) = \lim_{N_1'\to\infty}&\sum_{\mu_1'=1}^{N_1'}\sum_{\nu_1'=0}^{\mu_1'-1}\sum_{\sigma_1'=-\nu_1'}^{\nu_1'} \\ &V^{\alpha N_1^{\prime *}}_{p_1^{\prime *}q_1'}(\zeta_1',\zeta_1';\vec{R}_{ca})I_{p_1^{*}q_1'}(\zeta_1,\zeta_1';\vec{R}_{ab}) \ , \end{aligned} \tag{16}$$

$$I_{p_1^* p_1'^*;p_2^* p_2'^*}(\zeta_1,\zeta_1';\zeta_2,\zeta_2';\vec{R}_{ca},\vec{R}_{ba},\vec{R}_{da})$$

$$= \lim_{N_1',N_2,N_2'\to\infty} \sum_{\mu_1'=1}^{N_1'} \sum_{v_1'=0}^{\mu_1'-1} \sum_{\sigma_1'=-v_1'}^{v_1'} V_{p_1'^* q_1'}^{\alpha N_1'^*}(\zeta_1',\zeta_1';\vec{R}_{ca})$$

$$\times \sum_{\mu_2=1}^{N_2} \sum_{v_2=0}^{\mu_2-1} \sum_{\sigma_2=-v_2}^{v_2} V_{p_2^* q_2}^{\alpha N_2^*}(\zeta_2,\zeta_2;\vec{R}_{ba}) \sum_{\mu_2'=1}^{N_2'} \sum_{v_2'=0}^{\mu_2'-1} \sum_{\sigma_2'=-v_2'}^{v_2'}$$

$$\times V_{p_2'^* q_2'}^{\alpha N_2'^*}(\zeta_2',\zeta_2';\vec{R}_{da}) I_{p_1^* q_1' q_2 q_2'}(\zeta_1,\zeta_1';\zeta_2,\zeta_2') \quad , \tag{17}$$

where $q_1' \equiv \mu_1' v_1' \sigma_1'$, $q_2 \equiv \mu_2 v_2 \sigma_2$ $q_2' \equiv \mu_2' v_2' \sigma_2'$ and

$$I_{p_1^* p_1'^*}(\zeta_1,\zeta_1';\vec{R}_{ab}) \equiv I_{p_1^* p_1'^*}(\zeta_1,\zeta_1';0,\vec{R}_{ab})$$

$$= \int \chi_{p_1^*}^*(\zeta_1,\vec{r}_{a1}) \chi_{p_1'^*}(\zeta_1',\vec{r}_{a1}) \frac{1}{r_{b1}} \mathrm{d}V_1 \quad , \tag{18}$$

$$I_{p_1^* p_1'^*,p_2^* p_2'^*}(\zeta_1,\zeta_1',\zeta_2,\zeta_2') \equiv I_{p_1^* p_1'^*,p_2^* p_2'^*}(\zeta_1,\zeta_1',\zeta_2,\zeta_2';0,0,0)$$

$$= \int \chi_{p_1^*}^*(\zeta_1,\vec{r}_{a1}) \chi_{p_1'^*}(\zeta_1',\vec{r}_{a1}) \frac{1}{r_{21}}$$

$$\times \chi_{p_2^*}(\zeta_2,\vec{r}_{a2}) \chi_{p_2'^*}^*(\zeta_2',\vec{r}_{a2}) \mathrm{d}V_1 \mathrm{d}V_2 \tag{19}$$

It should be noted that using the orthonormality relation (Eq. 15), all the two-center Coulomb ($a \equiv c \neq b \equiv d$), two-center ($a \equiv c \equiv b \neq d$) and three-center ($a \equiv c \neq b \neq d$) hybrid and two-center ($a \equiv b \neq c \neq d$), three-center ($a \equiv b \neq c \neq d$), and four-center ($a \neq c \neq b \neq d$) electron-repulsion integrals can be calculated from Eq. (17).

3 Use of addition theorem for $\frac{1}{r_{21}}$

For the calculation of two-center nuclear-attraction and one-center electron-repulsion integrals we use in Eqs. (18) and (19) the expansion formula for the product of two spherical harmonics both with the same center [32]. Then we obtain

$$I_{p_1^* p_1'^*}(\zeta_1,\zeta_1';\vec{R}_{ab}) = \sum_{L_1=\left|l_1-l_1'\right|}^{l_1+l_1'} \sum_{M_1=-L_1}^{L_1} W_{p_1^* p_1'^* K_1^* L_1 M_1}(\zeta_1,\zeta_1',z_1)$$

$$\times J_{K_1^* L_1 M_1}(z_1,\vec{R}_{ab}) \quad , \tag{20}$$

$$I_{p_1^* p_1'^*;p_2^* p_2'^*}(\zeta_1,\zeta_1';\zeta_2,\zeta_2')$$

$$= \sum_{L_1=\left|l_1-l_1'\right|}^{l_1+l_1'} \sum_{M_1=-L_1}^{L_1} W_{p_1^* p_1'^* K_1^* L_1 M_1}(\zeta_1,\zeta_1',z_1)$$

$$\times \sum_{L_2=\left|l_2-l_2'\right|}^{l_2+l_2'} \sum_{M_2=-L_2}^{L_2} W_{p_2^* p_2'^* K_2^* L_2 M_2}(\zeta_2,\zeta_2',z_2)$$

$$\times J_{K_1^* L_1 M_1,K_2^* L_2 M_2}(z_1,z_2) \quad , \tag{21}$$

where $z_i = \zeta_i + \zeta_i'$, $t_i = (\zeta_i - \zeta_i')/(\zeta_i + \zeta_i')$, $K_i = n_i^* + n_i'^* - 1$ $(i = 1,2)$ and

$$W_{n_i^* l_i m_i, n_i'^* l_i' m_i', K_i^* L_i M_i}(\zeta_i,\zeta_i',z_i)$$

$$= \frac{z_i^{3/2}}{2^{K_i^*}} \left(\frac{\Gamma(2K_i^* + 1)}{2\Gamma(2n_i^* + 1)\Gamma(2n_i'^* + 1)} \right)^{1/2}$$

$$\times (1 + t_i)^{n_i^* + 1/2} (1 - t_i)^{n_i'^* + 1/2}$$

$$\times (2L_i + 1)^{1/2} C^{L_i|M_i|}(l_i m_i, l_i' m_i') A_{m_i m_i'}^{M_i} \quad , \tag{22}$$

$$J_{n_1^* l_1 m_1}(z_1,\vec{R}_{ab}) = \frac{1}{\sqrt{4\pi}} \int \chi_{n_1^* l_1 m_1}^*(z_1,\vec{r}_{a1}) \frac{1}{r_{b1}} \mathrm{d}V_1 \quad , \tag{23}$$

$$J_{n_1^* l_1 m_1, n_2^* l_2 m_2}(z_1,z_2)$$

$$= \frac{1}{4\pi} \int \chi_{n_1^* l_1 m_1}^*(z_1,\vec{r}_{a1}) \frac{1}{r_{21}} \chi_{n_2^* l_2 m_2}(z_2,\vec{r}_{a2}) \mathrm{d}V_1 \mathrm{d}V_2$$

$$= \frac{1}{\sqrt{4\pi}} \int J_{n_1^* l_1 m_1}(z_1,\vec{r}_{a2}) \chi_{n_2^* l_2 m_2}(z_2,\vec{r}_{a2}) \mathrm{d}V \quad . \tag{24}$$

Here $J_{n_1^* l_1 m_1}$ and $J_{n_1^* l_1 m_1, n_2^* l_2 m_2}$ are nuclear-attraction and electron-repulsion integrals, respectively. Thus, the multicenter integrals of ISTOs and NISTOs appearing in the Hartree–Fock–Roothaan equations for molecules are expressed through the basic integrals in Eqs. (23) and (24).

In order to calculate the basic integrals we use Eq. (1) for the Laplace expansion of the Coulomb potential in Eqs. (23) and (24). Then with the aid of the method set out in Ref. [30] we find for the two-center basic nuclear-attraction integrals the following analytical expression:

$$J_{n^* lm}(z,\vec{R}) = \begin{cases} 2^{n^*} \sqrt{\frac{2}{z}} \frac{\Gamma(n^*+1)}{\sqrt{\Gamma(2n^*+1)}} \delta_{l0} \delta_{m0} & \text{for } \vec{\mathrm{R}} = 0 \\ R_{n^* l}(z,R) S_{lm}(\theta,\varphi) & \text{for } \vec{\mathrm{R}} \neq 0 \end{cases} \tag{25}$$

where

$$R_{n^* l}(z,R)$$

$$= \frac{2^{n^*}}{2l+1} \sqrt{\frac{2}{z}} \frac{\Gamma(n^* + l + 2)}{\sqrt{\Gamma(2n^* + 1)}} \frac{1}{(zR)^{l+1}}$$

$$\times \left(1 - \frac{\Gamma(n^* + l + 2, zR)}{\Gamma(n^* + l + 2)} + \frac{(zR)^{2l+1} \Gamma(n^* - l + 1, zR)}{\Gamma(n^* + l + 2)} \right) . \tag{26}$$

Here $\Gamma(k,x)$ is the incomplete gamma function [29].

With the calculation of the one-center basic electron-repulsion integrals we use Eq.(25) in Eq. (24) and integrate over spherical angles of the second electron. Then using the results [29]

$$\Gamma(\alpha) = \gamma(\alpha,x) + \Gamma(\alpha,x) \quad , \tag{27}$$

$$\int_0^\infty x^{\mu-1} \mathrm{e}^{-\beta x} \gamma(v,\alpha x) \mathrm{d}x = \frac{\alpha^v \Gamma(\mu + v)}{v(\alpha + \beta)^{\mu+v}}$$

$$\times F\left(1, \mu + v; v + 1; \frac{\alpha}{\alpha + \beta}\right) \quad , \tag{28}$$

and

$$\int_0^\infty x^{\mu-1}\mathrm{e}^{-\beta x}\Gamma(v,\alpha x)\mathrm{d}x = \frac{\alpha^v\Gamma(\mu+v)}{\mu(\alpha+\beta)^{\mu+v}} \times F\left(1,\mu+v;\mu+1;\frac{\beta}{\alpha+\beta}\right) \qquad (29)$$

we get from Eq. (24)

$$J_{n_1^* l_1 m_1, n_2^* l_2 m_2}(z_1,z_2) = R_{n_1^* l_1, n_2^*}(z_1,z_2)\delta_{l_1 l_2}\delta_{m_1 m_2} \ , \qquad (30)$$

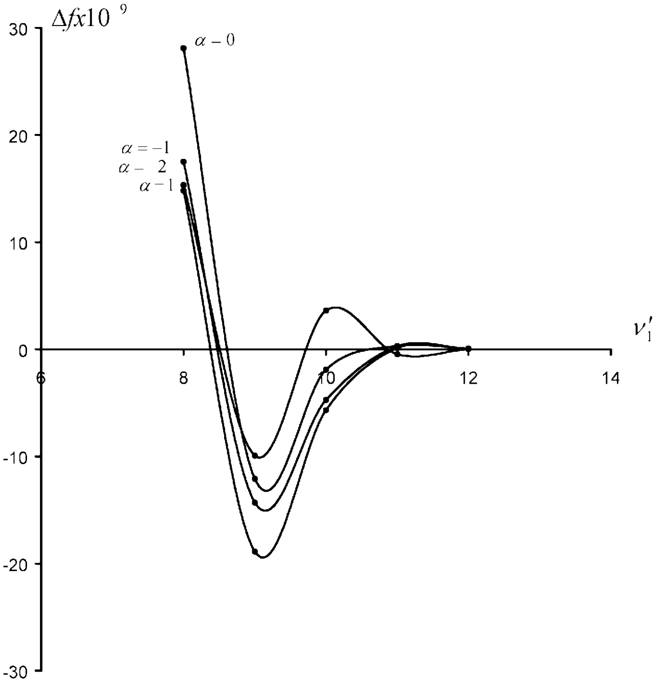

Fig. 1. The convergence of series in Eq. (16) for the three-center nuclear attraction integral $I_{3.521,3.311}$ with various values of α for translation of Slater-type orbitals (atomic units); $N_1{}' = 15$, $\sigma_1' = 5$, $\zeta = 4.6$, $\zeta' = 1.4$, $R_{\mathrm{ab}} = 1.8$, $\theta_{\mathrm{ab}} = 126°$, $\varphi_{\mathrm{ab}} = 315°$, $R_{\mathrm{ac}} = 2$, $\theta_{\mathrm{ac}} = 180°$, $\varphi_{\mathrm{ac}} = 215$

where

$$\begin{aligned} R_{n_1^* l_1, n_2^*}(z_1,z_2) &= \int_0^\infty R_{n_1^* l_1}(z_1,r)R_{n_2^*}(z_2,r)r^2\mathrm{d}r \\ &= \frac{2^{n_1^*+n_2^*+1}\Gamma(n_1^*+n_2^*+3)}{(2l_1+1)[\Gamma(2n_1^*+1)\Gamma(2n_2^*+1)]^{1/2}} \\ &\times \frac{\eta^{n_2^*+1/2}}{z_1^2(1+\eta)^{n_1^*+n_2^*+3}}\left(\frac{F\left(1,n_1^*+n_2^*+3;n_1^*+l_1+3,\frac{1}{1+\eta}\right)}{n_1^*+l_1+2}\right. \\ &+ \left.\frac{F\left(1,n_1^*+n_2^*+3;n_2^*+l_1+3,\frac{\eta}{1+\eta}\right)}{n_2^*+l_1+2}\right) \ . \end{aligned} \qquad (31)$$

Here $\eta = z_2/z_1$ and F is the hypergeometric function determined by

$$F(\alpha,\beta;\gamma;x) = \sum_{k=0}^{\infty}\frac{(\alpha)_k(\beta)_k}{(\gamma)_k}\frac{x^k}{k!} \ , \qquad (32)$$

where

$$(\alpha)_0 = 1, (\alpha)_n = \alpha(\alpha+1)\ldots(\alpha+n-1) = \frac{\Gamma(\alpha+n)}{\Gamma(\alpha)} \ . \qquad (33)$$

As can be seen from Eqs. (25), (26), (30), and (31), the two-center nuclear-attraction and one-center electron-repulsion basic integrals are expressed through the gamma and hypergeometric functions, several procedures for the evaluation of which can be found in the literature [33].

The accuracy of computer results for the two- and three-center nuclear-attraction integrals with STOs can be determined by the use of spherically symmetrical or

Table 1. The values of two-center nuclear attraction integrals over integer and noninteger n Slater-type orbitals obtained in the molecular (lined-up and non-lined-up) coordinate system (atomic units)

n^*	l	m	ζ	N'^*	l'	m'	ζ'	R	θ	φ	Eq. (20)	Δf
2	1	0	10.8	2	1	0	5.3	5.4	20	90	$1.35970293363843 \times 10^{-1}$	20
2.15	1	0	12.8	2.7	1	0	8.5	5.4	30	120	$1.42535414658415 \times 10^{-1}$	19
3	2	2	7.12	2	1	1	3.8	10.5	10	60	$-1.80415671180953 \times 10^{-4}$	19
3.5	2	2	9.7	2.78	1	1	9.7	10.5	10	60	$-1.27099610692958 \times 10^{-4}$	19
4	3	2	15.9	5	3	3	10.7	15.5	40	30	$-4.65385676682645 \times 10^{-6}$	21
4.77	3	2	18.5	5.45	3	3	8.1	21.5	50	150	$9.89161909073411 \times 10^{-7}$	21
6	4	4	14.8	6	5	5	20.8	25.1	60	180	$1.98425009417673 \times 10^{-4}$	18
6.4	4	4	14.4	6.7	5	5	25.8	32.5	60	180	$8.25827340203041 \times 10^{-5}$	18
8	7	7	21.4	7	6	6	20.8	53.2	70	210	$5.16357446188277 \times 10^{-5}$	17
8.25	7	7	25.1	7.6	6	6	18.2	75.3	70	210	$2.38053768054153 \times 10^{-5}$	18
10	9	−7	12.5	10	8	−8	10.2	100.7	80	240	$-1.58615189629610 \times 10^{-6}$	19
10.45	9	−7	15.2	10.4	8	−8	8.1	100.7	80	240	$-6.27670149239174 \times 10^{-7}$	18
15	13	13	31.5	14	13	13	23.8	0.7	0	0	$9.64834293778156 \times 10^{-1}$	18
15.6	13	13	35.5	14.8	13	13	20.8	0.5	0	0	$5.50364514764564 \times 10^{-1}$	17
25	24	24	15.5	25	24	24	10.4	15.5	36	36	$2.34470131643294 \times 10^{-2}$	18
25.6	24	24	12.3	25.2	24	24	9.6	18.5	36	36	$3.79963686060315 \times 10^{-2}$	17
40	20	20	9.2	40	20	20	9.2	8.5	54	144	$1.17546693251303 \times 10^{-2}$	16
40.5	20	20	12.9	40.3	20	20	7.9	12.8	108	288	$7.30477020966995 \times 10^{-3}$	16
50	21	20	12.9	50	21	20	7.9	38	126	324	$1.30238004549549 \times 10^{-3}$	15
50.6	21	20	9.4	50.8	21	20	6.7	38	126	324	$5.90189696138292 \times 10^{-3}$	15

Table 2. Comparison of methods of computing three-center nuclear-attraction integrals, noninteger n Slater-type orbitals, obtained in the molecular (lined-up and non-lined-up) coordinate system (atomic units); $N_1' = 15$, $v_1' = 14$, $\sigma_1' = 5$

n^*	l	m	ζ	n'^*	l'	m'	ζ'	R_{ac}	θ_{ac}	φ_{ac}	R_{ab}	θ_{ab}	φ_{ab}	Eq (16)		
														$\alpha = 0$	$\alpha = 1$	$\alpha = -1$
2	1	0	9.4	2	1	0	6.7	2.2	30	45	1.2	60	36	$-9.5730491028 \times 10^{-5}$	$-9.5730483230 \times 10^{-5}$	$-9.5730481674 \times 10^{-5}$
2.6	1	0	5.9	2.8	1	0	3.6	0.2	30	45	0.8	60	36	$8.0290672567 \times 10^{-1}$	$8.0290651740 \times 10^{-1}$	$8.0290407055 \times 10^{-1}$
2	1	1	6.5	2	1	1	4.3	0.7	60	135	1.1	90	72	$6.2979231317 \times 10^{-2}$	$6.2979439297 \times 10^{-2}$	$6.2979339754 \times 10^{-2}$
2.24	1	1	6.6	2.56	1	1	7.4	0.7	60	135	1.1	120	108	$1.1480343178 \times 10^{-2}$	$1.1480361160 \times 10^{-2}$	$1.1480559348 \times 10^{-2}$
2	1	−1	8.6	2	1	1	3.7	0.4	90	180	1.8	150	144	$-1.1329879799 \times 10^{-2}$	$-1.1329878054 \times 10^{-2}$	$-1.1329885664 \times 10^{-2}$
2.87	1	−1	10.8	2.66	1	1	5.3	0.4	120	225	1.8	180	180	$-7.7754429087 \times 10^{-2}$	$-7.7754429266 \times 10^{-2}$	$-7.7754427537 \times 10^{-2}$
2.7	1	−1	6.7	2.3	1	−1	4.5	1.4	150	270	1.5	108	216	$-1.8401726323 \times 10^{-3}$	$-1.8401730584 \times 10^{-3}$	$-1.8401555994 \times 10^{-3}$

Table 3. Comparison of methods of computing one-center, two-center Coulomb and two-center hybrid integrals, noninteger n Slater-type orbitals, obtained in the molecular (lined-up and non-lined-up) coordinate system (atomic units); $N_1 = N_1' = 12$, $v_2 = v_2' = 11$, $\sigma_2 = \sigma_2' = 5$, $\theta_{ba} = 120°$, $\varphi_{ba} = 144°$, $\theta_{da} = 45°$, $\varphi_{da} = 150°$

n_1	l_1	m_1	ζ_1	n'^*_1	l'_1	m'_1	ζ'_1	n^*_2	l_2	m_2	ζ_2	n'^*_2	l'_2	m'_2	ζ'_2	R_{ba}	R_{da}	Eq. (17)		
																		$\alpha = 0$	$\alpha = 1$	$\alpha = -1$
2.3	1	1	7.3	2.3	1	1	7.3	3.6	1	1	4.6	2.5	1	1	8.6	0	0	$9.4538618174 \times 10^{-1}$		
3.5	2	2	12.7	3.5	2	2	12.7	3.5	2	2	12.7	3.7	2	2	4.2	0	0	$6.2337917676 \times 10^{-1}$		
4.3	3	2	9.1	3.5	2	2	7.4	4.3	3	2	9.1	3.5	2	2	7.4	0	0	$2.4620956487 \times 10^{-1}$		
5.4	4	3	7.9	5.4	4	3	7.9	5.4	4	3	7.9	6.6	4	3	4.1	0	0	$3.1377045718 \times 10^{-1}$		
10.5	8	6	9.7	10.5	8	6	9.7	10.5	8	6	9.7	10.5	8	6	9.7	0	0	$8.3958156592 \times 10^{-1}$		
2.5	1	0	7.5	2.5	1	0	7.5	2.5	1	0	7.5	2.8	1	0	8.7	0	1.4	$-2.6312401180 \times 10^{-2}$	$-2.6312424618 \times 10^{-2}$	$-2.6312413094 \times 10^{-2}$
2.8	1	1	6.8	2.8	1	1	6.8	2.8	1	1	6.8	2.3	1	1	4.5	0	1.6	$-9.4749167886 \times 10^{-2}$	$-9.4749149433 \times 10^{-2}$	$-9.4749175693 \times 10^{-2}$
2.78	1	−1	4.6	2.78	1	−1	4.6	2.78	1	−1	4.6	2.63	1	−1	6.2	0	0.8	$3.4521171339 \times 10^{-1}$	$3.4521172619 \times 10^{-1}$	$3.4521175224 \times 10^{-1}$
3.8	1	1	6.4	3.8	1	1	6.4	3.8	1	1	6.4	3.6	1	1	8.6	0	0.6	$3.6951779907 \times 10^{-1}$	$3.6951779803 \times 10^{-1}$	$3.6951776576 \times 10^{-1}$
2.38	1	0	7.6	2.38	1	0	7.6	2.46	1	0	9.8	2.46	1	0	9.8	0.8	0	$9.8340995977 \times 10^{-1}$	$9.8340830914 \times 10^{-1}$	$9.8340894917 \times 10^{-1}$
2.8	1	1	4.5	2.8	1	1	4.5	2.6	1	0	5.6	2.6	1	0	5.6	1.1	0	$5.7987538464 \times 10^{-1}$	$5.7987554076 \times 10^{-1}$	$5.7987550239 \times 10^{-1}$
2.5	1	1	3.4	2.5	1	1	3.4	2.1	1	1	1.5	2.1	1	1	1.5	0.9	0	$4.7866999462 \times 10^{-1}$	$4.7866971371 \times 10^{-1}$	$4.7866978744 \times 10^{-1}$
2.7	1	−1	5.3	2.7	1	−1	5.3	2.9	1	−1	3.1	2.9	1	−1	3.1	0.5	0	$6.7503032897 \times 10^{-1}$	$6.7503044306 \times 10^{-1}$	$6.7503171956 \times 10^{-1}$

angular independence properties (see Eqs.15, 16 in Ref. [34]),

$$\sum_{m=-l}^{l} I_{klm,k'l'm'}(\zeta,\zeta';R,\theta,\varphi) = \sum_{\lambda=0}^{l} \frac{2}{1+\delta_{\lambda 0}} \times I_{kl\lambda,k'l'\lambda}(\zeta,\zeta';R,0,0)\ , \tag{34}$$

$$\sum_{m=-l}^{l} \sum_{m'=-l'}^{l'} \left| I_{klm,k'l'm'}(\zeta,\zeta';R,\theta,\varphi) \right|^2 = \sum_{\lambda=0}^{\min(l,l')} \frac{2}{1+\delta_{\lambda 0}} \left| I_{kl\lambda,k'l'\lambda}(\zeta,\zeta';R,0,0) \right|^2\ , \tag{35}$$

and different sets of expansion formulas (Eqs. 16, 17) for $\alpha = 1,\ 0,\ -1,\ -2,..,.$ respectively. Here $k = n^*, n$ and $k' = n'^*, n'$.

4 Numerical results and discussion

As can be seen from Eqs. (16) and (17) and Eqs. (20) and (21), the overlap, basic nuclear-attraction, and electron-repulsion integrals occur in the multicenter nuclear-attraction and electron-repulsion integrals over STOs. The computer programs presented in Refs. [26, 27, 28] for overlap integrals are used in this study. On the basis of analytical relations (Eqs. 25, 26, 30, 31, 32) for the basic integrals and series expansion formulas (Eqs. 16, 17) for the multicenter integrals we also constructed a program. This program can be used in the calculation of multicenter nuclear-attraction and electron-repulsion integrals over ISTOs and NISTOs with arbitrary values of parameters.

In Fig. 1, for $\lambda < N$–1 we present the convergence of series in Eq. (16) obtained using coefficients (Eqs. 11, 12) for expansion of real ISTOs and NISTOs. Here λ is the upper limit of the indices v_1' and v_2'.The series accuracy $\Delta f_\lambda = f_{N-1} - f_\lambda$ for the three-center nuclear-attraction integrals is shown in Fig. 1, where the quantities f_{N-1} are the values of integrals for $\lambda = N-1$. We see that the convergence of the series with respect to v_1' and v_2' is rapid; therefore, we can include only a few terms obtained from the summations over indices v_1' and v_2'. The full lines in Fig. 1 represent the results of calculations made using Eqs. (11) and (12), obtained from Ψ^{-2}-ETOs, Ψ^{-1}-ETOs, Ψ^{0}-ETOs, and Ψ^{-1}-ETOs, respectively.

The computation time required for the calculation of multicenter nuclear-attraction and electron-repulsion integrals is not given in the tables owing to the fact that the comparison cannot be made with the different computers used in other work. It is seen from the algorithm presented for multicenter integrals that our computation times are satisfactory. For instance, for two-center nuclear-attraction integrals with quantum sets $n^* = 25.6$, $l = 24$, $m = 24$, $\zeta = 12.3$, $n'^* = 25.2$, $l' = 24$, $m' = 24$, $\zeta' = 9.6$ and $R_{\mathrm{ab}} = 18.5$, $\theta_{\mathrm{ab}} = 36°$, $\varphi_{\mathrm{ab}} = 36$, the computation time is about 0.6 ms.

The results of the calculations in atomic units for the two-center, three-center nuclear-attraction, one-center, two-center Coulomb, and two-center hybrid electron-repulsion integrals obtained with a Pentium 233 MHz computer (using TURBO PASCAL 7.0 language) are represented in Tables 1, 2, and 3, respectively. The comparative values obtained from Eqs. (11) and (12) with the expansion of different Ψ^{α}-ETOs are shown in these tables. We see from the tables that the accuracy of the computer results for different expansion formulas obtained from Ψ^{-1}-ETOs, Ψ^{0}-ETOs, and Ψ^{-1}-ETOs is satisfactory.

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